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The Impact of Sulfate-Reducing Bacteria on Welded Copper-Nickel Seawater Piping Systems

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Field and laboratory experiments were designed to evaluate corrosion in welds and heat-affected zones in copper/nickel seawater piping systems exposed to estuarine water and seawater. The localized corrosion was shown to be due to the following sequence of events: 1) metal segregation during heating processes; 2) settlement of sulfide-producing bacteria in welds; 3) sulfide derivatization; 4) disruption of the surface films by turbulence and 5) formation of adjacent cathodic and anodic areas.

Metallic segregation in welded areas was detected by an X-ray spectrometer before the welds were exposed to estuarine water. Within the crevices, occlusions, and surface irregularities of butt and socket welds unique environments of microbial colonization existed. The sulfate-reducing bacteria (SRB) population in the weld areas was 1×10^4 cm^{-2}. In the presence of in situ production of sulfides, copper- and nickel-enriched areas were susceptible to sulfide derivatization; however, surface deposits on the nickel-enriched areas were easily removed by turbulence. The sulfide-coated, copper-enriched areas were cathodic relative to the adjacent nickel-enriched areas, thus resulting in selective attack.

$FeSO_4$ and Na_2SO_3 were evaluated as inhibitors of the localized attack. Fe^{++} (50 ppb) did not alter the attack of sulfides, but SO_3^{--} (10 ppm) did lessen the observed attack.

Introduction

The potential problem of sulfide-induced accelerated corrosion of copper-nickel piping systems in ships constructed in estuarine waters has been recognized for 15 years. Although much progress has been made in recognizing the causes and effects of such corrosion in pipe sections and/or plate sections, few investigations have addressed corrosion at welds or the adjacent heat-affected zones. That the phenomenon of accelerated corrosion at or near to welds has received little attention is somewhat surprising; where detected, accelerated pitting corrosion attributed to sulfide attack occurs predominantly close to flanges or elbows (Figure 1). Further, sulfide-induced pitting occurs only rarely upstream of flanges or elbows. Because most, if not all, flanges and elbows contain welds (and/or braze joints), studying welds under field and laboratory conditions seems justified.

The major justifications for not studying welds and heat-affected zones include the peculiarities of particular welds in terms of the thicknesses of the metal welded, the types of joint made, and the masses and geometries of the surrounding base plate in relation to heating and cooling rates. In other words, generalities regarding welds may or may not be of general significance since each weld is, to some extent, unique. In light of these caveats, this paper presents a study of the corrosion in various types of experimental and construction welds exposed to estuarine water and synthetic salt solutions containing SRBs or dissolved sulfides under field and laboratory conditions.

Experimental Procedure

Welded sections employed in this study consisted of nominal 90:10 Cu/Ni (CDA 706) shipyard production pipe with normal production weld filler consisting of nominal 70:30 Cu/Ni (CDA 710) rod. Beads, fillets, and welds were gas tungsten arc welded (GTAW) with 70:30 Cu/Ni filler at 50-150 A using normal shipyard production techniques. In-

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FIGURE 1
Pitted pipe sections removed from Cu/Ni seawater piping systems.

FIGURE 2
Interior of an external bead welded 90/100 copper-nickel pipe.

ternal inerting of the pipe sections was not employed. Surface chemical analyses were performed with a KEVEX-7000 energy-dispersive X-ray spectrometer (EDXA) coupled to an AMRay™ 1000A scanning electron microscope (SEM). Subsections were sputter-coated with gold before photography with the SEM.

The following configurations were used:

1. Externally bead-welded 2-7/8 in. OD x 2-3/4 in. ID (wall thickness 0.091 + 0.004 in.) pipe (Figure 2).
2. Socket-welded 4-7/16 in. OD x 4-1/8 in. ID (wall thickness 0.123 +/- 0.004 in.) pipe with the sleeve 4-5/8 in. OD x 4-1/2 in. ID. the overlapping "outer" sleeve (Figure 3) was 70:30 Cu/Ni; the inner member was 90:10 Cu/Ni.
3. Single "V" butt-jointed 2-7/8 in. OD x 2-3/4 in. ID (wall thickness 0.091 + 0.004 in.) pipe (Figure 4).

Details on the field and laboratory experiments are given in CORROSION/88 Paper No. 81 by the authors. (A complete set of references is also given in this paper.)

Results

Field Experiments

Figure 5 is a schematic of the field experiments discussed in this section. In these experiments, water temperature varied from 9 C to 30 C over the experimental period, which extended from September 1986 to September 1987. The pH varied from 7.4 to 8.2. Chlorinity varied from 4.3 to 20.0 ppt Cl^-. Chlorinity can be converted to salinity using the following relationship: Salinity (ppt) = 1.806 Chlorinity (ppt Cl^-). Total suspended solids ranged from 10 ppm to 65 ppm during dredging operations. Dissolved oxygen varied from 4.3 ppm

FIGURE 3
Internal and external views of socket-welded 90/10 copper-nickel pipe.

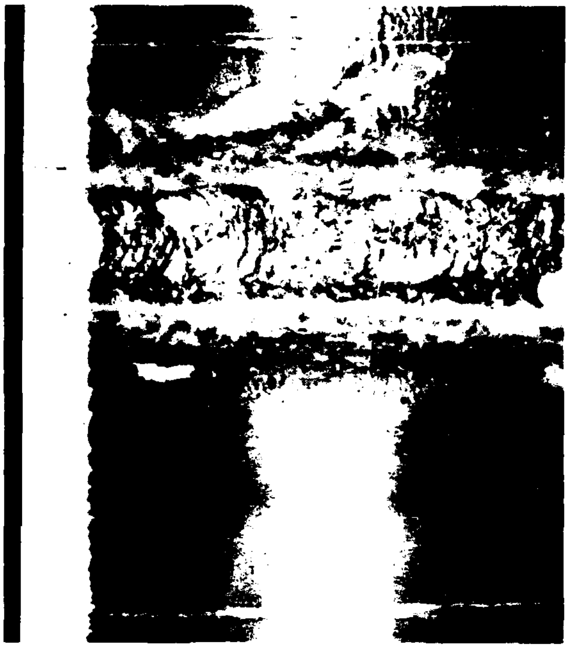

FIGURE 4
Interior view of butt-welded 90/10 copper-nickel pipe.

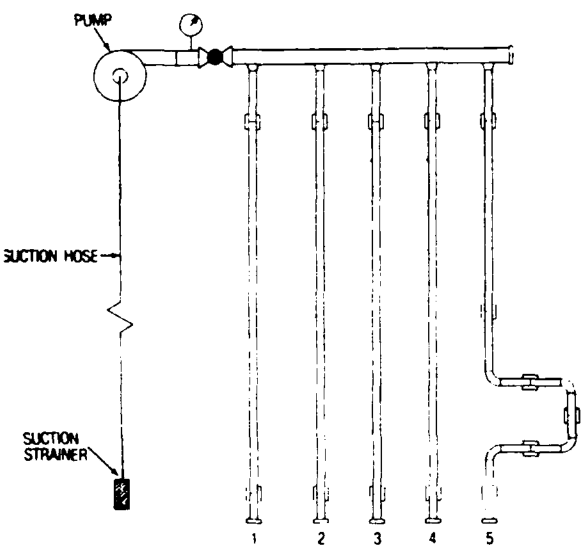

FIGURE 5
Flow diagram for field experiment: Section 5 contains external bead, butt and socket welds, socket brazings, and bends.

during July to 10.5 ppm in late December. Copper and iron concentrations in the river water fluctuated between 5 and 70 ppb and between 150 and 906 ppb, respectively. Ferrous ion concentrations in the intake water were typically 70 ppb ± 5. Dissolved sulfides could not be detected during the experiment. The mean concentration for sulfates (SO_4^{-2}) was $\approx$2500 mg/l. The mean total organic

FIGURE 6
Cross section of epoxy-embedded butt weld before exposure.

carbon concentration was 10 $\pm$ 2 mg/l. Standard plate counts indicated bacterial populations of 1 x 10^4 – 10^5 per cc. The concentration of SRBs in the estuarine water was 1 x 10^2 – 10^3 per cc.

The welded areas were characterized by crevice and surface irregularities prior to exposure (Figure 6). The welds were heavily colonized by SRBs with an estimated population of 1 x 10^4 cm^{-2} in the weld areas (Figures 7). The sulfide production rate was determined to be 0.5 $\mu gcm^{-2}d^{-1}$. In all cases the welded sections were pitted downstream from the weld (Figure 8).

Laboratory Experiments

The weld root and adjacent flow zone of butt-welded samples exposed to 50 ppm sulfide became coated with a thick, black, uniform, highly adherent layer (Cu_2S) after the first addition of aerated sulfide (Figure 9). EDAX analysis indicated the main components of these zones are copper and sulfur, with little, if any, nickel content. The adjacent nickel-rich zones also blacken (nickel and sulfur by EDAX analysis), but upon exposure to fresh artificial seawater under flowing conditions, the nickel-rich zones were rapidly spalled down to fresh metal (still nickel-enriched) while the weld root and flow zones are relatively unaffected (Figure 10).

The loosely adherent "flakes" at the extremes of the visually heat-affected zone are blackened in the sulfide treatment and rapidly spall off the surface under flow conditions to expose a fresh metal (copper-colored) surface. With each repetition of sulfide addition, the surface blackening recurs and with each repetition of fresh synthetic seawater flow the nickel-rich areas adjacent to the weld root are stripped down to fresh metal. During the three sulfide repetitions, the metal distribution in the weld root, the flow zone, and the adjacent zone remained abnormal, that is the weld root and flow zone remain copper enriched and the adjacent area is nickel enriched relative to the parent samples (non-heat affected).

The externally bead-welded (experimental "weld" in the sense that the bead was nonpenetrating, yet visually heat-affected zones virtually identical to normal butt-welded samples were observed) and socket-welded samples exhibited behavior similar to that discussed above for butt-welded samples, where corresponding zones existed between the different welds. Specifically, nickel-enriched zones were first darkened by sulfide addition (as low as 1 ppm) and were subsequently "cleaned" by fresh artificial seawater under flow conditions. Similarly, the "flakey" zones remote from the locus of the external weld seam were originally blackened by sulfide, but the action of fresh-flowing liquid spalled this material from the surface. It is interesting to note that one run, which employed 50-ppb ferrous ion relative to another run was, for all intents and purposes, identical to the other run. Further, by EDAX analysis, no enhancement of surface iron content of the run with 50 ppb ferrous ion existed.

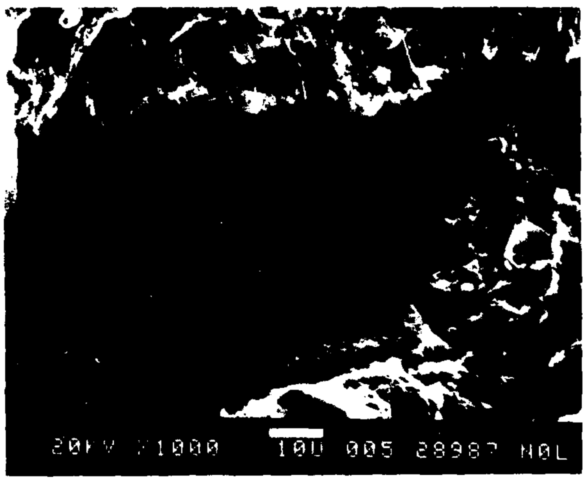

FIGURE 7
Bacterial filaments within cracked surface film on weld area.

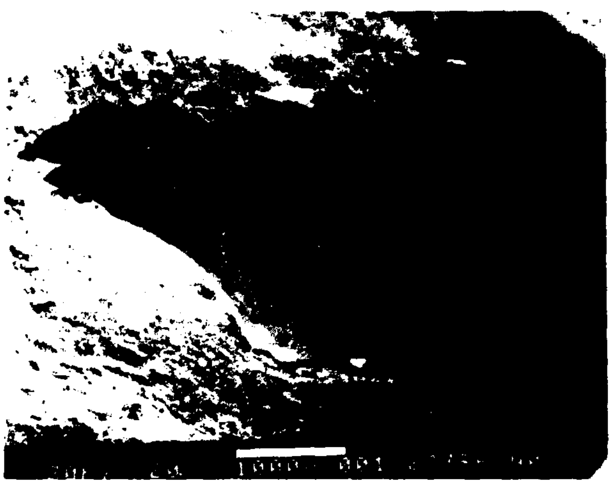

FIGURE 8
Pit downstram of colonized weld.

The socket-welded samples employed in still another run, which involved addition of 10 ppm sulfite (as sodium sulfite) to the flowing liquid, exhibited EDAX spectra similar to those observed in the runs mentioned above, with the exception that the sulfur content was depressed.

Discussion

Surface metallic segregation on the inner (weld root and/or visually heat-affected) surface of 90/10 Cu/Ni pipes in the process of butt welding, external bead welding, and external socket welding has been previously reported.[1] For example, the weld root and an immediately adjacent flow zone in butt-welded samples was markedly enriched in copper relative to the parent plate (pipe). Adjacent to the flow zone, the surface metal was markedly enriched in nickel relative to the parent plate, and at distances as great as 1.5 in. from some butt welds the surface composition was altered relative to the parent plate.

Loosely adherent "flakes" enriched in copper relative to the parent plate overlaid nickel-enriched surfaces at the outer regions of the visually heat-affected zone. Numerous zones could be observed in butt and externally welded samples. These zones can be correlated when the weld root is ignored.

Syrett[2] suggested a mechanism for accelerated corrosion of copper alloys in sulfide-polluted seawa-

FIGURE 9
Butt weld discolored by addition of 50 ppm sulfide to 35 ppt SIS.

FIGURE 10
Butt weld after exposure to 50 ppm sulfide in 35 ppt SIS, followed by fresh-flowing SIS

ter that has as its essential features:

1. rapid surface deposition of sulfide when the normal copper-oxide film is contacted by deaerated sulfide solutions;
2. random surface spalling of sulfide film upon exposure of sulfide layered alloy to fresh, aerated seawater to produce areas of underlying oxide and/or base plate;
3. rapid formation of protective oxide film in areas where surface spalling has occurred that results in reduced ("normal") corrosion rates; and
4. accelerated corrosion under sulfide deposits caused by relatively less rapid protective oxide films being produced under such surface deposits.

While we would agree with this mechanism for the non-heat-affected areas of the pipe, additional considerations must be applied to corrosion near-weld seams and the adjacent heat-affected zones. First, the thick, copper (oxide)-enriched films on weld roots and the adjacent flow zone were rapidly converted to thick, strongly adherent copper sulfide-enriched films upon exposure to sulfide. These films were very strongly adherent in fresh, aerated seawater.

Secondly, the areas where sulfide layer spalling occurred were remote from the weld root, leading to exposed metal or oxide layers near the heavily coated weld root. If the weld root and flow zone are [illegible] by an overlaying oxide/sulfide film, [illegible] should be cathodic under aerobic conditions to the proximate bare metal surfacemetal oxide areas. Thus, for the welding procedures described, accelerated sulfide-induced corrosion should occur predominantly near to, but not at, the weld seam itself. Numerous samples of failed pipe specimens from naval vessels documented this pattern relative to the bulk of the pipe.

Sulfide-accelerated corrosion can occur in waters with immeasurably small sulfide concentrations in the presence of SRBs. SRBs are obligate anaerobic bacteria that can use sulfate, present in estuarine and marine waters as a terminal electron acceptor in place of oxygen and thus reduce the sulfate to sulfide. Weld roots have highly irregular, porous surfaces that facilitate bacterial colonization. In anaerobic niches within the biofilm, SRBs produce sulfide, which impinges on the weld seam surface, the adjacent flow zone, and the downstream surface of the heat-affected zone. Exposure of such sulfide-insulted surfaces to fresh, aerated seawater results in the rapid spalling of surface deposits on the downstream side of weld seams, rendering these surfaces anodic to the sulfide-coated weld root. The result is accelerated corrosion predominantly on the downstream side of the weld in the heat-affected zone.

Hack[3] reported that $FeSO_4$ additions (50 ppm Fe^{++}) prevented sulfide-induced corrosion of copper-nickel alloys by stripping corrosive sulfides from the solution before reaction with the pipe surface was possible. However, in these laboratory experiments, ferrous ion (50 ppb) did not alter the attack of sulfide on the heat-affected zones. The possibility that SO_3^{--} additions may lessen the severity of sulfide attack is currently being evaluated.

Conclusions

1. The surface characteristics of the welds and heat-affected zones of Cu/Ni weldments are different from that of non-heat-affected Cu/Ni alloys.
2. Welds provide unique environments for the colonization of sulfate-reducing bacteria.
3. Selective sulfide reactions occur within the weld and heat-affected zones of Cu/Ni weldments, thus resulting in selective attack.
4. The addition of ferrous ion at 50 ppb does not appear to alter the attack of sulfide on the various heat-affected zones.
5. Sulfite additions of 10 ppm appear to lessen sulfide attack.

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3. H. P. Hack, "Effectiveness of Ferrous Sulfate as an Inhibitor for Sulfide-Induced Corrosion of Copper-Nickel Alloys," DTNSRDC/77-0072, 1977.

This article is a modified version of Paper No. 81, CORROSION/88, St. Louis, MO.